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SYNTHESIS AND THIN FILM ASSEMBLY OF COPPER NANOPARTICLES FOR SENSING CONTAMINANTS IN AIRCRAFT CABINS

Chuan-Jian Zhong
Derrick M. Mott
Peter N. Njoki
Lingyan Y. Wang
Jin Luo

State University of New York

George W. Miller

Air Force Research Laboratory

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**Air Force Research Laboratory
Human Effectiveness Directorate
Biosciences and Protection Division
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14. ABSTRACT
Nanoparticle-structured thin films with tunable electronic properties provide an advanced solution for the design of chemical sensing materials. The exploitation of such sensing nanomaterials for chemical sensors in monitoring aircraft cabin contaminants requires the ability to fine tune the nanostructure in terms of size, shape, composition, spacing, functionality, and stability. This report describes the findings of an investigation that developed a method to synthesize copper nanoparticles of controlled size and surface properties and a process to assemble the nanoparticles into chemiresistive sensing thin films. The approach involved the manipulation of temperature in the synthesis of monolayer-capped copper nanoparticles and the interparticle binding chemistry for a controlled thin film assembly. The chemiresistive sensing properties of the nanostructured thin films were demonstrated in response to a volatile organic compound (benzene) and a toxic gas (carbon monoxide). These findings constitute the basis for the synthesis and assembly of a variety of copper nanoparticle-based advanced sensing materials.

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Abstract

Nanoparticle-structured thin films with tunable electronic properties provide an advanced solution for the design of chemical sensing materials. The exploitation of such sensing nanomaterials for chemical sensors in monitoring aircraft cabin contaminants requires the ability to fine tune the nanostructure in terms of size, shape, composition, spacing, functionality, and stability. This report describes the findings of an investigation aimed at developing a method to synthesize copper nanoparticles of controlled size and surface properties; and developing a process to assemble the nanoparticles into chemiresistive sensing thin films. Our approach involves the manipulation of temperature in the synthesis of monolayer-capped copper nanoparticles and the interparticle binding chemistry for a controlled thin film assembly. One element of this approach is the exploration of size-dependent nanoparticle melting-point decrease for temperature regulation of size and shape, and another element involves the exploitation of amine, carboxylate and thiolate based copper binding chemistry to mediate the thin film assemblies with controlled interparticle spacing and functionality. The viability of these two elements and the chemiresisitve sensing properties of the nanostructured thin films in response to a volatile organic compound (benzene) and a toxic gas (carbon monoxide) has been demonstrated. These findings constitute the basis for the synthesis and assembly of a variety of copper nanoparticle-based advanced sensing materials.

Introduction

Thin film assemblies of gold and gold-silver alloy nanoparticles have been demonstrated for sensor/biosensor applications largely due to the abilities of nano-engineering gold in a dimension of a few nanometers. In contrast, the lack of well-established capabilities to synthesize copper nanoparticles in a few nanometer diameters is perhaps one of the biggest obstacles to the use of copper in emerging nanotechnology applications. Currently, the synthesis of size- and shape-controlled copper nanoparticles is difficult due to the propensity for surface oxidation and the limited understanding of the nanoscale surface chemistry. In view of the many distinctive perspectives of copper in terms of electrical properties and low cost, the development of a capability for nano-engineering size, composition, and surface properties of copper nanoparticles and thin film assemblies is expected to advance the design of sensing materials in many significant ways which are currently dominated by gold, silver, and platinum nanoparticles. To this end, copper nanoparticles must be produced with controllable sizes, shapes and surface properties, and the nanoparticles must be assembled into thin films using molecularly-designed interparticle chemistry. It is the goal of the proposed project to demonstrate the feasibility of synthesis and assembly of two-component monolayer capped copper nanoparticles. The basic principle for such sensing nanomaterials exploits the chemiresistive responses of the nanoparticle films by tunable interparticle spacing, dielectrics, and particle sizes, with the added value of low cost and copper-specific chemical properties.

Air Force Relevance. The relevance of the proposed synthesis of copper nanoparticles and their thin film assembly to the USAF is in developing advanced sensing materials and miniaturized devices for monitoring contaminants in aircraft cabins.

Hypothesis. The basic hypothesis of the proposed work exploits amine- and/or carboxylate-copper binding chemistry for molecularly-engineered encapsulation and assembly of copper nanoparticles. There are two key elements in this hypothesis. One involves synthesis of copper nanoparticles with a two-component monolayer encapsulation consisting of amine and
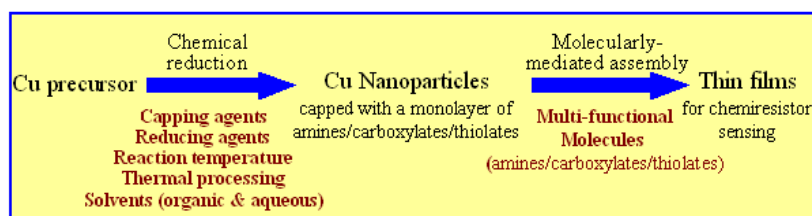
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carboxylate capping molecules. The other element involves the use of α,ω-bifunctional linker molecules such as diamines (e.g., $H_2N\text{-}(CH_2)_n\text{-}NH_2$) and dicarboxylic acids (e.g., $HO_2C\text{-}(CH_2)_n\text{-}CO_2H$) to mediate the thin film assembly of copper nanoparticles with controlled interparticle properties via selective interparticle binding using $-NH_2$ and/or $-CO_2^-$ ligand exchange-crosslinking chemistry. The demonstration of the feasibility of these two entirely new concepts could form the basis of producing a variety of metal or oxide nanoparticle thin film assemblies. The proposed work will benefit from our previous and on-going research experiences in synthesis and assembly of gold, platinum, silver, and bimetallic/trimetallic alloy nanoparticles, and lead to cost-effective production of novel sensing nanomaterials. In the past few months, we have carried out investigations in testing the hypothesis, and have made significant progress toward achieving our objectives. The methods used in our investigations and the results are described in the following sections.

Methods

The following two major methods have been used in our investigations to demonstrate the feasibility of the hypothesis.

1. Synthesis of Cu nanoparticles with oleyl amine and oleic acid capping by manipulation of reaction temperature. This approach is based on previous work by State University New York (SUNY) Binghamton and others in the synthesis of alloy (PtFe, PtVFe) or iron oxide nanoparticles with oleyl amine and oleic acid, as capping agents. By expanding it to the synthesis of Cu nanoparticles, size control will be achieved by manipulating the feeding ratio of the capping agents and the reaction temperature. The temperature-controlled size and shape growth is an innovative element of this approach because we envision the size-dependent melting point decrease of nanoparticles will allow temperature regulation of the growth in size and shape. The correlation between temperature and size/shape/surface properties will be the focus of our investigation.

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2. Assembly of Cu nanoparticles into thin films via selective interparticle binding using α, ω bifunctional linkers. This approach is based on SUNY Binghamton previous work using α, ω-bifunctional linker molecules, such as, dithiols and dicarboxylic acids to assemble gold and gold-silver alloy nanoparticles. For the thin film assembly of Cu nanoparticles, the use of dicarboxylic acids and diamines for the interparticle binding chemistry is an innovative element of this approach, because it involves selective interparticle $-NH_2$ and/or $-CO_2^-$ exchange-crosslinking chemistry to mediate assembly of two-component monolayer capped nanoparticles, and could lead to a variety of thin films with controlled interparticle spacing and tunable functionality. In addition to studying the mechanistic details of the interparticle chemistry, the charge transfer mechanism will also be studied by measuring the conductivity-temperature relationship. Scheme 1 outlines the general flow of our approaches and methods used in our investigations. The results from the investigation of these approaches will constitute the basis for the synthesis and assembly of a variety of transition metal nanoparticles for advanced thin film sensing nanomaterials.

Scheme 1. An illustration of the flow of our investigations in the synthesis of copper nanoparticles, and the preparation of thin film assembly for chemiresistor sensors.

Results and Discussion

1. Synthesis of copper nanoparticles

We have developed two routes to synthesize Cu nanoparticles: one involving the use of separate reducing and capping agents (e.g., 1,2-hexadecanediol, oleyl amine and oleic acid), and the other using a single reducing/capping agent (e.g., oleyl amine). We also demonstrated the viability of thermally-controlled evolution of the as-synthesized nanoparticles in solutions in

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terms of sizes, shapes, and surface composition. In particular, we focused on the thermal processing of the amine-capped copper nanoparticles towards defined particle sizes and shapes and surface characterization of the resulting particles. The surface characterization is aimed at understanding the surface structure of the capping shells and the surface oxidation states of the copper nanoparticle cores. The understanding of the oxidation states allowed us to evaluate the stability of the nanoparticles in air.

As shown in Scheme 2, route A involves the use of both reducing and capping agents, whereas Route B involves the use of only a single reducing/capping agent.

Scheme 2. Two chemical reduction routes: (A) using both reducing and capping agents, and (B) using only a single reducing/capping agents. [Cu(acac)$_2$ = Cu(II) acetylacetonate]

One of the key elements in the synthesis of the molecularly-capped copper nanoparticles involved manipulation of reaction temperature in octylether solvent in the presence of oleyl amine and oleic acid capping agents and 1,2-hexadecanediol reducing agent. For example, a solution of Cu(II) acetylacetonate (20 mM) with 1,2-hexadecanediol (a reducing agent) (60 mM) was heated under argon to a temperature of 105 °C with stirring. Oleic acid and oleyl amine capping agents were added to the solution (20 mM each). The solution was heated to higher temperatures (150 °C) and kept at the temperature for 30 minutes. The resulting particles were yellow in color and suspended well in hexane or toluene. Figure 1 shows a

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representative set of Transmission Electron Microscopy (TEM) images of the nanoparticle samples.
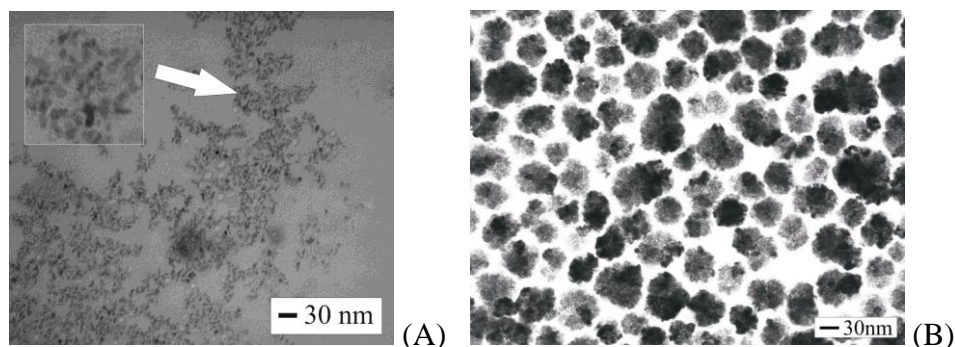

Figure 1. TEM images of the as-synthesized copper nanoparticles capped with 50/50 oleic acid and oleyl amine synthesized at 150 °C (A) and 155 °C (B) (Route A).

The morphologies of the nanoparticles depended on the reaction conditions, especially the temperature. For nanoparticles capped with 50/50 oleic acid and oleyl amine which were synthesized at 155 °C and washed to remove excess capping agent, the particles were yellow in color and remained suspended. For nanoparticles capped with oleyl amine only synthesized at 155 °C, they appeared yellow, and remained suspended for several weeks. Thermal Gravimetric Analysis (TGA) was used to assess the composition of the capping structure. For 6-nm sized copper nanoparticles, the mass decrease due to the removal of the capping agents was found to take place in the range of 150 - 300 ℃. The mass ratio of capping molecules to the copper particles showed ~39% capping shell and 61% copper mass. For a 50/50 mixture of the oleic acid/oleyl amine capping molecules on a 6-nm copper nanoparticle, a spherical model calculation[2] yields 24% for the capping materials. The deviation from the theoretical value could be partially due to residual octyl ether in the sample[2].

By manipulating the reaction temperature and reaction time in route B synthesis, we were able to vary the sizes and morphologies of the resulting nanoparticles. Figure 2 shows a set of TEM images for several samples of Cu nanoparticles thus produced. These data show that the particle sizes can be manipulated by controlling a combination of the reaction temperature,

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reaction time, and capping/reducing agents. Particles with sizes ranging from 6 nm to 50 nm have been synthesized.
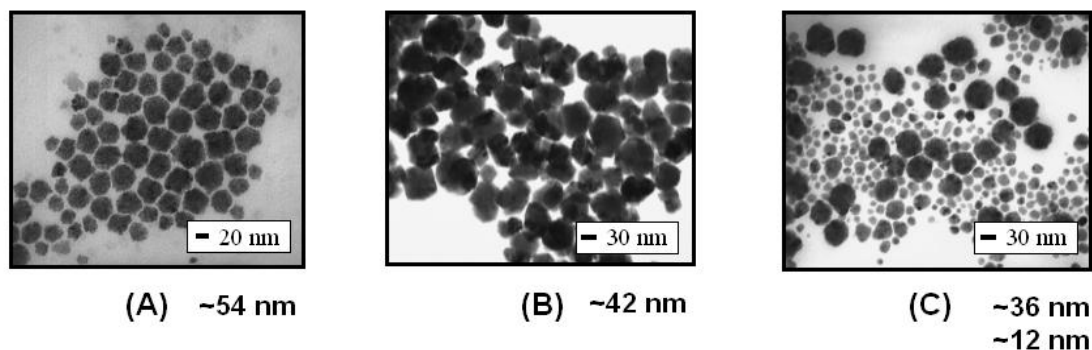

Figure 2. TEM micrographs showing Cu nanoparticles formed via different methods: (A) using only oleyl amine as capping/reducing agent (route-B) at 165 $^{\circ}$C; (B) using only oleyl amine capping/reducing agent (route-B) at 165 ºC for 6 hours; and (C) using only oleyl amine capping/reducing agent (route-B) at 155 °C for 6 hours.

In contrast to the temperature manipulation in the synthesis reaction, we have also examined the viability of thermally-controlled evolution of the as-synthesized nanoparticles in terms of sizes, shapes, and surface composition. This process is essentially a post-synthesis treatment. The basic concept of this processing route stems from the previous work demonstrating the synthesis of different gold and alloy nanoparticles (e.g., FePt nanoparticles[1], PtVFe nanoparticles[2]), and takes advantage of the effect of particle sizes on the melting temperature of nanoparticles under the reaction conditions (e.g., Au nanoparticles[3]). The thermal processing has been demonstrated in our laboratory for processing gold and alloy nanoparticles to controlled sizes and monodispersity [3]. The theoretical calculation of melting temperature vs. particle sizes for Cu particles (Figure 3) shows that the melting temperature drops dramatically as size decreases to a few nm. This physical phenomenon constitutes the basis for the thermal processing because the surface melting temperature is believed to be even lower so that the processing can occur under mild heating conditions in a solution. In addition to the theoretical basis for the decreased melting point of nanoscale copper particles, there are experimental studies indicating that nanoscale copper materials exhibit depressed melting points[3-4].
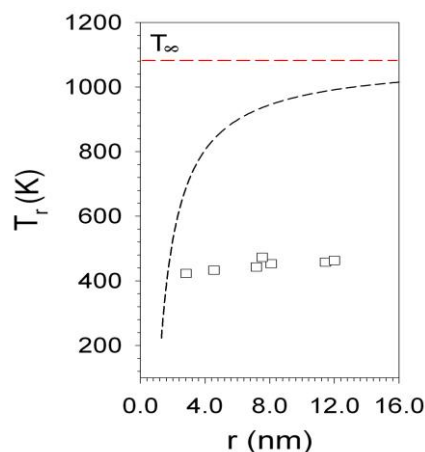
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Figure 3. Theoretical modeling of the melting temperature of copper nanoparticles as a function of particle radius based on the equation: $\dfrac{T_r - T_\infty}{T_\infty} = -\dfrac{4}{\rho_s L 2r}\left[\gamma_s - \gamma_l\left(\dfrac{\rho_s}{\rho_l}\right)^{2/3}\right]$. The parameters used for the theoretical calculation were $\rho_s = 8960$, $\rho_l = 8020$ kg/m2, L = 20500 J/Kg4, $\gamma_s = 1.29$, and $\gamma_l = 1.11$ J/m2 [3e]. The actual temperatures used in the synthesis vs. particle size are included as square points.

By controlling a combination of the reaction temperature, reaction time, and capping/reducing agents, the amine-capped or thiolate-capped Cu nanoparticles with small sizes (1-2 nm) were obtained first. The particles were then used as precursors to undergo thermally-controlled evolution in solutions of well-defined constituents. The thermal processing permitted changes of the particles in terms of sizes, shapes, and surface composition depending on the thermal treatment conditions. The basic concept of this processing route takes advantage of the effect of particle sizes on the melting temperature of nanoparticles under the reaction conditions. The phenomenon that the melting temperature drops dramatically as size decreases to a few nm constitutes the basis for the thermal processing. Scheme 3 shows the general scheme for the synthesis of thiolate-capped Cu nanoparticles and subsequent thermal processing to the larger-sized and shaped nanoparticles.

(A)

(B)

Scheme 3. The general schemes illustrating the two-phase synthesis of thiolate-capped Cu nanoparticles (TOABr: tetraoctylammonium bromide) (A) and the subsequent thermal processing to form larger-sized and shaped nanoparticles (B).

Figure 4A shows a representative set of TEM micrographs for Cu nanoparticles produced via thermally-controlled evolution of the decanethiols (DT)-capped Cu nanoparticles at 130 ^{0}C. The precursor Cu nanoparticles (~1 nm) were synthesized by chemical reduction of $CuCl_2$ in toluene solution in the presence of tetraoctylammonium bromide (TOABr) and decanethiols (DT). The thermal processing protocol is shown to be quite effective in controlling the size and shape of the Cu nanoparticles. Figure 4B shows another set of TEM micrographs with higher resolution. The as-synthesized particles appear very small (~1 nm). Depending on the temperature and processing time, the particles are shown to increase in size or to exhibit rod-like shape. The nanorods obtained by the 2hr-processing time appear to be highly monodispersed in diameters (4-5 nm), and vary in length (10-20 nm). The presence of the ordered domains of the nanorods and the range of the interparticle distance are consistent with the presence of the capping shell materials. This finding is very interesting because it provides us with an effective means to tune the particle size and shape.

A close examination of some of the large-sized particles seems to reveal subtle cluster features, hinting at the possibility of coalescence of smaller-sized particles or dendritic growth of

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the particles. It is known that the growth of nanoparticles is influenced by the strength of absorption of the encapsulating ligands and the competition between the interparticle aggregation for the growth of the particles and the molecular encapsulation for their stabilization.
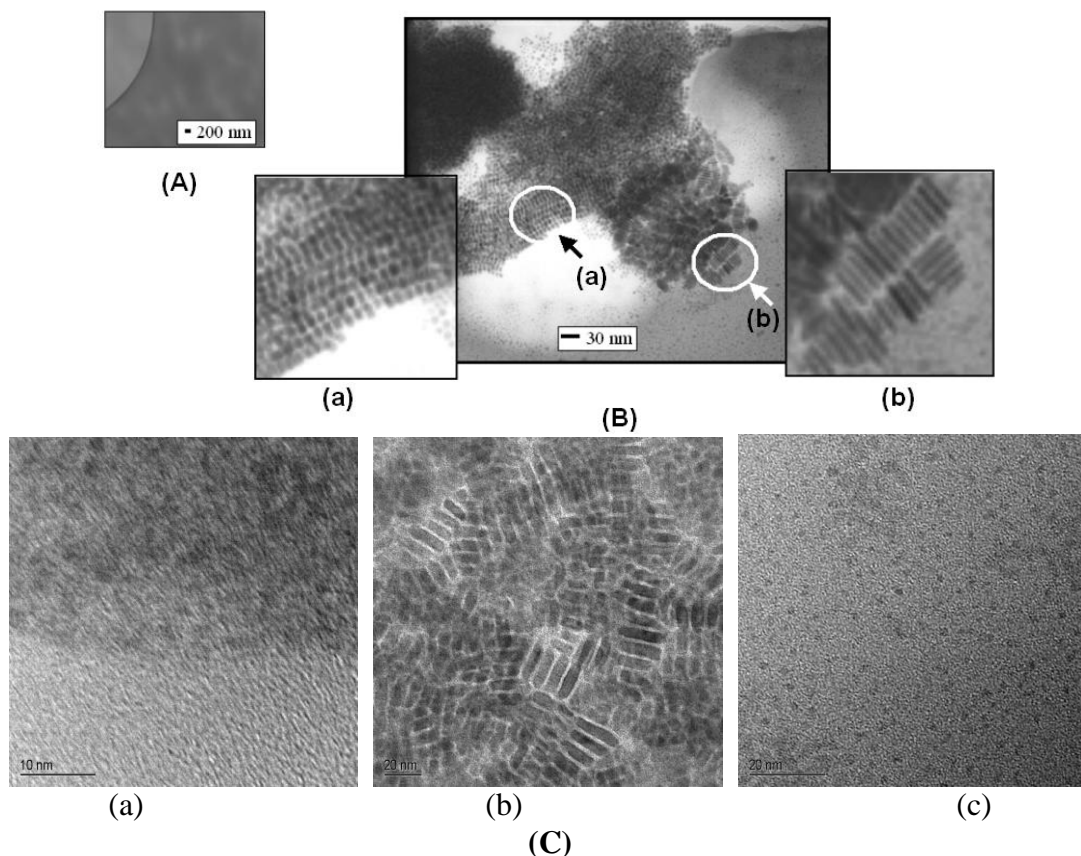

Figure 4. TEM micrographs. (A and B): Cu nanoparticles formed via thermally-controlled evolution of the as-synthesized nanoparticles. The as-synthesized Cu nanoparticles (A) were made by chemical reduction of CuCl$_2$ in toluene solution. The processed product (B) displays nanorods ((a) L: ~7 nm, W ~3 nm; (b) L ~22 nm, W ~3 nm) and nanoparticles (~5 nm). (C) A representative set of TEM micrographs for the as-synthesized DT-capped Cu nanoparticles (a), and thermally-evolved DT-capped Cu nanoparticles at 130 $^{\circ}$C for 2 hrs (b), and for 1 hr (c).

We have also performed X-ray photoelectron spectroscopic (XPS) analysis to analyze the chemical nature and composition of the capping shells and the surface properties of the copper nanocrystal cores. By spectral comparison (Figure 5), one set of doublet peaks characteristic of Cu(2p), i.e., 933.1 eV for Cu2p3/2 and 954.0 eV for Cu2p1/2, is identified for the thermally-evolved (2 hrs) Cu nanoparticles. This observation is in contrast to the as-synthesized amine-capped Cu nanoparticles (Figure 5A top) and the thermally-processed amine-capped Cu nanoparticles (Figure 5A bottom), which reveal two sets of doublet peaks: one set showing 932.5

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eV for Cu2p$_{3/2}$ and 953.0 eV for Cu2p$_{1/2}$, and the other showing 932.5 eV for Cu2p$_{3/2}$, and 953.0 eV for Cu2p$_{1/2}$. This contrast is believed to reflect the presence of copper oxides on the nanocrystal surfaces for the amine-capped nanoparticles. It is evident that the thermal processing not only evolves the size and shape, but also prevents the formation of oxides on the particle surface depending on the structure of the capping molecules. The latter is supported by the absence of Cu2p bands corresponding to copper oxides in the XPS spectra. Furthermore, the detection of the S2p band (Figure 5 (B)) and the detection of the N1s band (Figure 5 (C)) confirm the capping shell structures of thiolates for the DT-capped Cu nanoparticles and amines for the amine-capped Cu nanoparticles.
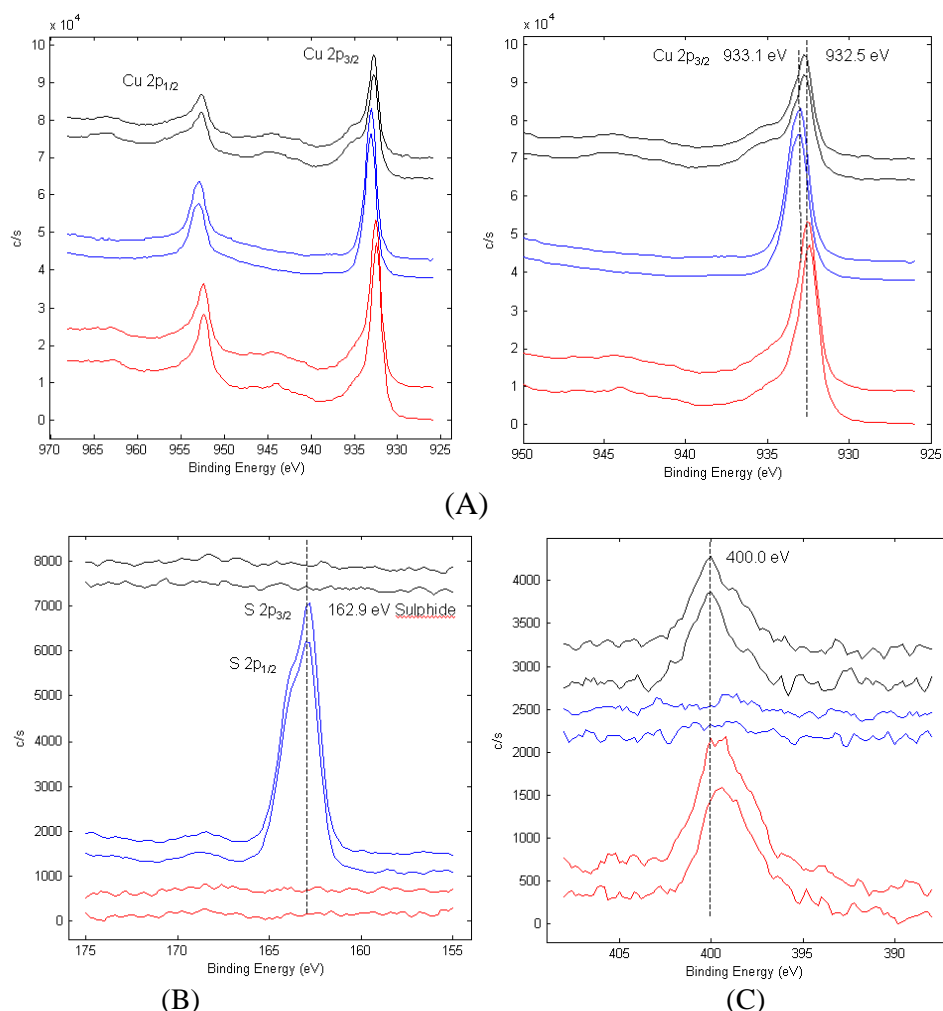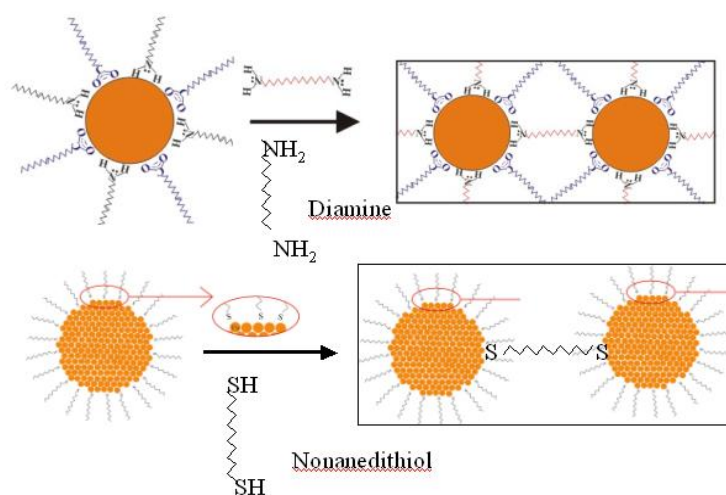

Figure 5. XPS spectra in the Cu2p (A), S2p (B) and N1s (C) regions. Black curves: As-synthesized amine-capped Cu nanoparticles; Blue curves: thermally-processed DT-capped Cu nanoparticles in decanethiol (DT)-containing solution for 2 hrs.; Red curves: thermally-processed amine-capped Cu nanoparticles in the solution for 1 hr. For each sample, two repetitions of the measurements were recorded.

The thermal processing protocol is shown to be quite effective in controlling the size and shape of the thiolate-capped Cu nanoparticles depending on the temperature and processing time. In contrast to the presence of copper oxides on the nanocrystal surfaces for the amine-capped nanoparticles, the DT-capped Cu nanoparticles not only evolve in size and shape in the thermal processing, but also eliminate the formation of oxides on the particle surface. This finding is important because stability of Cu nanoparticles in air is critical for the exploitation of the electrical conductivity properties of the nanoparticles in the targeted chemical sensing application.

2. Assembly of Cu nanoparticles

To demonstrate the viability of the thin film formation from copper nanoparticles, we investigated a number of different bifunctional molecules as linkers for the assembly on different substrates. Scheme 4 illustrates our approaches to the assembly of Cu nanoparticles using two different linker molecules, diamines and dithiols.

Scheme 4. Schemes showing two approaches to the assembly of nanoparticles using two different linker molecules: diamines (top) and dithiols (bottom).

Using dithiols or diamines, the formation of thin films on glass substrates were observed. The films exhibited yellow to green colors depending on particle sizes, linker

molecules, and film thickness. Figure 6 shows a representative photo of diaminodecane-mediated thin film assembly of Cu nanoparticles capped with oleyl amines applied at gap of Interdigitated Microelectrode (IME).

Figure 6. Photo of diaminodecane-mediated thin film assembly of Cu nanoparticles capped with oleyl amines applied at gap of Interdigitated Microelectrode (IME).
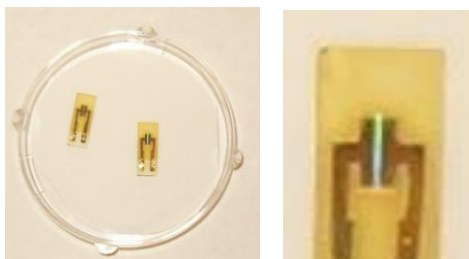
3. Testing of chemiresistor sensing properties of Cu nanoparticle thin films

The choice of Cu nanoparticles as sensing materials is based on a number of considerations. First of all, we understand that the ability of nanostructured materials to respond to a specific contaminant is dependent on structural characteristics, such as size, shape, composition, and spacing. Second, thin film assemblies of gold and gold-silver alloy nanoparticles have been demonstrated in sensor applications. Third, in comparison with gold nanoparticles, there is a lack of established methods to synthesize copper nanoparticles. Fourth, copper nanoparticle properties and low cost may potentially lead to an advancement in the design of sensor materials. Finally, we envision the creation of an array of "sensors-on-a-chip" to identify and quantify multiple contaminants, and such advanced nanostructured sensors could be used as sensing materials for monitoring aircraft cabins for harmful contaminants and potentially predict aircraft subsystem failures. Figure 7A shows the basic concept of chemiresistor sensing for thin film assembly of Cu nanoparticles (NDT-Cu) on IME device.

Figure 7B-C shows a preliminary set of data for the chemirresistor sensor responses to benzene (Bz) vapor for thin film assembly of Cu nanoparticles (NDT-Cu) on IME device. The response profile displays a negative sign (i.e., resistance decreases upon exposure to Bz). The response sensitivity can be obtained from the slope of the linear regression of the $\Delta R/R$ vs.

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concentration plot. In this case, the value of the response sensitivity obtained was 3×10^{-4} ppm^{-1}.

In comparison, the response sensitivity is 5×10^{-5} for NDT-Au (2nm) film, and 3×10^{-4} ppm^{-1} for
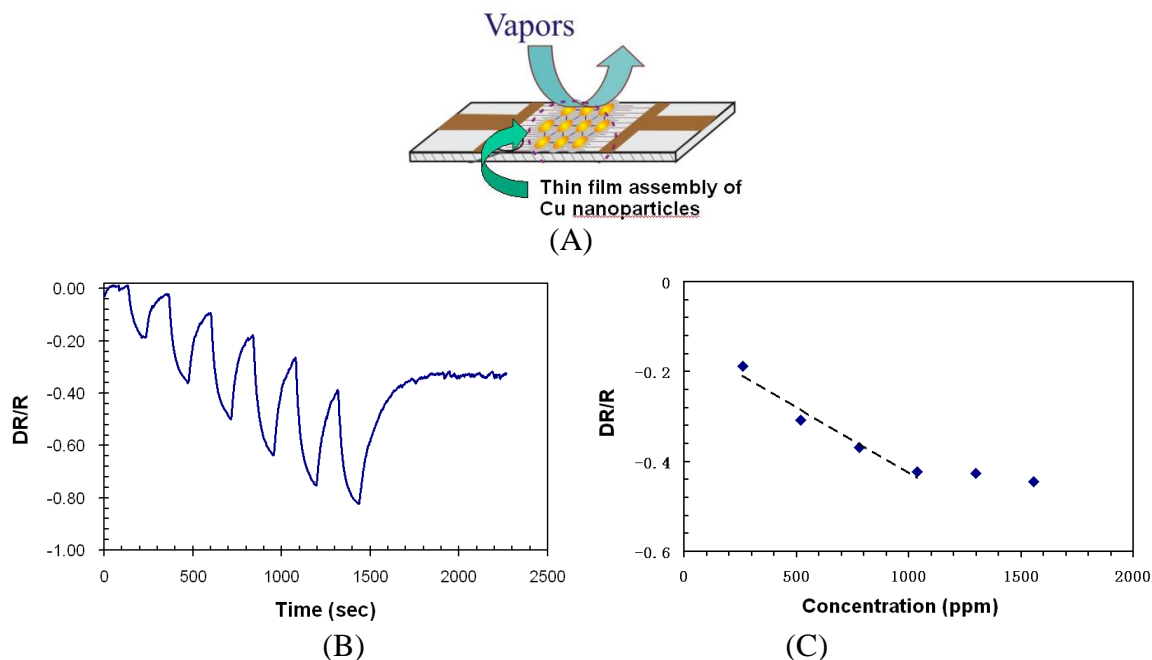
MUA-Au(2nm) film.

Figure 7. Thin film assembly (A), sensor response profiles (B), and response sensitivity plot (C) to benzene (Bz) vapor (vapor concentrations from left to right: 260, 519, 779, 1038, 1298, and 1558 ppm) for a thin film assembly of Cu nanoparticles (NDT-Cu) on IME device. Response profile displays a negative sign (i.e., resistance decreases upon exposure to Bz). Linear regression: $Y = -3.0\times10^{-4}X - 1.3\times10^{-1}$ ($R^2 = 9.6\times10^{-1}$). The response sensitivity is 3×10^{-4} ppm^{-1}.

Figure 8 shows another set of preliminary data to illustrate the sensing properties of Cu-

based films (NDT-Cu$_{nm}$) to carbon monoxide (CO) gas. The basic sensing mechanism involves

binding of CO on the exposed Cu-nanocrystal binding sites of the thin film assemblies.
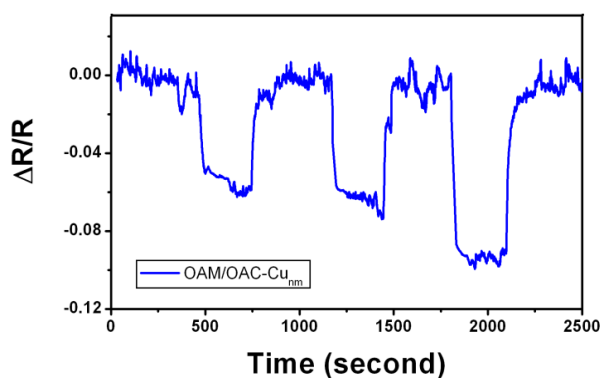
Figure 8. Response profiles to CO gas of different concentrations (CO: 0. 75% (1300 ppm), 1.0% (1600 ppm), and 1.25% (1900 ppm) in N_2) for an IME device coated with the assembly of copper nanoparticles (~5 nm) using nonanedithiol linking molecules (NDT-Cu$_{nm}$).

An important finding is that the response profiles depend on the structural nature of the linking molecules and the composition of the nanocrystals. In contrast to the often-observed increase in $\Delta R/R$ upon exposure to analytes, the response profile for NDT-Cu$_{nm}$ thin film features a decrease in $\Delta R/R$ upon exposure to CO and a return to baseline upon purge with nitrogen.

Conclusions

In conclusion, we have shown that copper nanoparticles with controlled size, shape, stability, and solubility in organic solvents can be synthesized by manipulating reaction temperature. Copper nanoparticles have been synthesized with various sizes, shapes (e.g., rods and cubes), and solubility in organic and aqueous solvents. Copper nanoparticles encapsulated with oleyl amine or decanethiolate monolayers are stable in ambient conditions. Dithiol and diamine molecules have been demonstrated for mediating thin film assembly of copper nanoparticles. The electrical properties of the thin films are dependent on linking molecules and nanocrystal composition. Initial testing with benzene and carbon monoxide showed the feasibility of using Cu nanoparticle thin film assemblies as sensing materials. The response profiles appear dependent on the structural nature of the linking molecules and the nanocrystal composition. These results are promising in demonstrating the feasibility of the synthesis and assembly of copper nanoparticles and their use as chemiresistor sensing films for detecting gases/vapors. A manuscript is also in preparation reporting some of the results [5].

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References.

[1]   Sun, S.; Murray, C. B.; Weller, D.; Folks, L.; Moser, A. *Science* 2000, *278*, 1989.

[2]   Luo, J.; Han, L.; Kariuki, N. N.; Wang, L.; Mott, D.; Zhong C. J.; He, T. *Chem. Mater.* 2005, *17*, 5282.

[3]   (a) Maye, M. M.; Zheng, W. X.; Leibowitz, F. L.; Ly, N. K.; Zhong, C. J. *Langmuir*, 2000, *16*, 490. (b) M. J. Schadt, W. Cheung, J. Luo, C. J. Zhong, *Chem. Mater*. 2006, *18,* 5147. (c) D. Mott, J. Galkowski, L. Wang, J. Luo, C. J. Zhong, Langmuir, 2007, 23, 5740-5745. (d) H. Y. Park, M. J. Schadt, L. Wang, I-Im S. Lim, P. N. Njoki, S. H. Kim, M.-Y. Jang, J. Luo, C. J. Zhong, Langmuir, 2007, *23*, 9050-9056. (e) D. Mott, J. Galkowski, L. Wang, J. Luo, C. J. Zhong, *Langmuir*, 2007, 23, 5740-5745.

[4]   Karabacak, T.; DeLuca, J. S.; Wang, P.-I.; Ten Eyck, G. A.; Ye, D.; Wang, G.-C.; Lu, T.-M. *J. Appl. Phys.* 2006, *99*, 064394.

[5]   D. Mott, J. Yin, M. Engelhard, C. Wang, P. Njoki, P. Chang, L. Wang, J. Luo, C. J. Zhong, G. Miller, Manuscript in preparation.